REMOVAL OF PERCHLORATE FROM A CONTAMINATED GROUNDWATER IN THE LAS VEGAS VALLEY USING ION-EXCHANGE RESINS.

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INTRODUCTION

Perchlorate (ClO_4^-), an important component of rocket fuel and explosives, has been detected widely and in high concentrations in the Las Vegas Valley, Nevada. The Kerr McGee Chemical Corporation (KMCC) and the Pacific Engineering and Production (Pepcon), located in the Basic Management Industrial (BMI) complex, have produced perchlorate since 1945 in Henderson, Nevada. Perchlorate containing-wastes, discharged into unlined ponds, have migrated through the soils to the groundwater in this area. The contaminated groundwater reaches the Las Vegas Wash through an alluvial channel. The Las Vegas Wash is a stream that discharges into Lake Mead, in the Colorado River, which is the drinking water source for 1.2 million residents of the Las Vegas Valley and millions of people in California and Arizona. Several wells in the BMI complex contain perchlorate concentrations as high as 3,700 mg/L. In the Las Vegas Wash perchlorate concentrations vary from 0.5 to 1.0 mg/L and in Lake Mead perchlorate concentrations vary from 0.005 to 0.015 mg/L (5 to 15 ppb).

Several technologies are currently under investigation for their potential to remove perchlorate from waters. Strong base anions exchange resins have proven to be very effective in removing perchlorate from synthetic perchlorate solutions. However, the competition between perchlorate and other anions, contained in "real" waters has not been fully investigated. This study evaluates the removal of perchlorate by ion exchange resins from a contaminated groundwater in the Las Vegas Valley. In this paper, the term "real" refers to the contaminated water from the Las Vegas Valley.

EXPERIMENTAL

Both strong base anion-exchange (SBAX) and weak base anion exchange (WBAX) resins were investigated for their ability to remove perchlorate from the contaminated water. Resins manufactured by Sybron Chemicals and Purolite were used. Figures 1A and 1B show the experimental set-ups for resin testing. In Figure 1B, up-flow regeneration of loaded columns can be observed. The tests were performed in 15 and 22 mm ID fixed-bed glass columns with bed height of approximately one foot. The resins were supported by glass beads. Peristaltic pumps were used to feed and backwash the columns. The contaminated water or synthetic perchlorate solutions were fed to the columns in a down-flow mode. The effluent from the columns was collected at determined time intervals and analyzed for perchlorate and other anions of interest. Regeneration was executed in an up-flow mode, with either sodium chloride (12%) or caustic solutions. Perchlorate and anions analyses were performed using a Dionex-120 ion chromatograph. Table I shows the concentration of solutions used in the test.

Ion Exchange Testing for Perchlorate Removal at UNLV

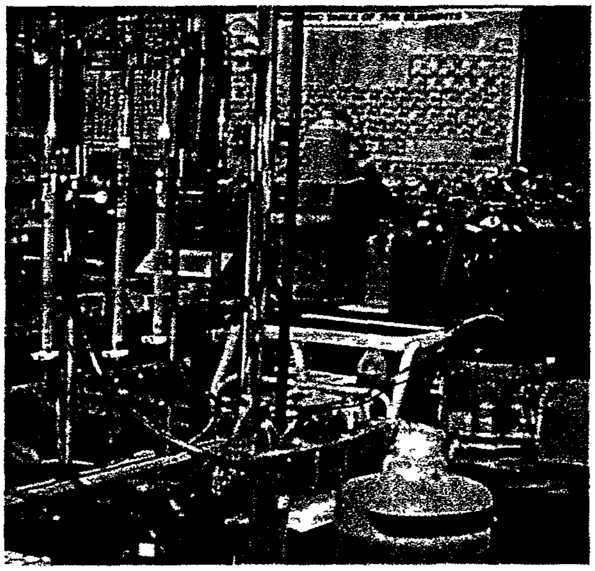

Figure 1A

Figure 1B

Table I: Water samples used in the study.

Synthetic Solution:	**"Real" Water**
Perchlorate (ClO_4^-) = 40 mg/L	Perchlorate (ClO_4^-) = 80 mg/L Nitrate (NO_3^-) = 50 mg/L Sulfate (SO_4^{2-}) = 2000 mg/L

RESULTS AND ANALYSIS

Table II shows the concentration of major anions for several water samples used in the resin testing. Notice that perchlorate concentrations average 80 mg/L. Sulfate and nitrate concentrations average 2000 and 50 mg/L, respectively.

Table II: Concentration of major anions in the "real" water.

	Concentrations (mg/L)								
	Bottle #								**Aver.**
Chem.	1	2	3	4	5	6	7	8	
ClO_4^-	79.95	78.15	80.27	78.84	80.67	78.87	82.45	84.36	**80.45**
NO_3^-	57.84	50.10	50.88	50.68	50.88	50.18	51.68	51.30	**51.69**
SO_4^{2-}	2094	2083	2052	2088	2059	2091	2077	2080	**2078**

Figure 2 shows the breakthrough curve for a strong-base styrenic type I resin (Sybron Chemicals – ASB1) loaded with synthetic perchlorate soltition and loaded with the "real" water. Notice that the column utilization for the synthetic solution was 100% while for the "real" water it was only 48%. This indicates that approximately 50% of the resin capacity were occupied by anions other than perchlorate. However, observe that sulfate and nitrate did not exchange much. Therefore, there may exist another explanation for the lower resin capacity. It was noticed that the resin column in which the "real" water was run became very dark, suggesting the presence of humic substances (Figure 3).

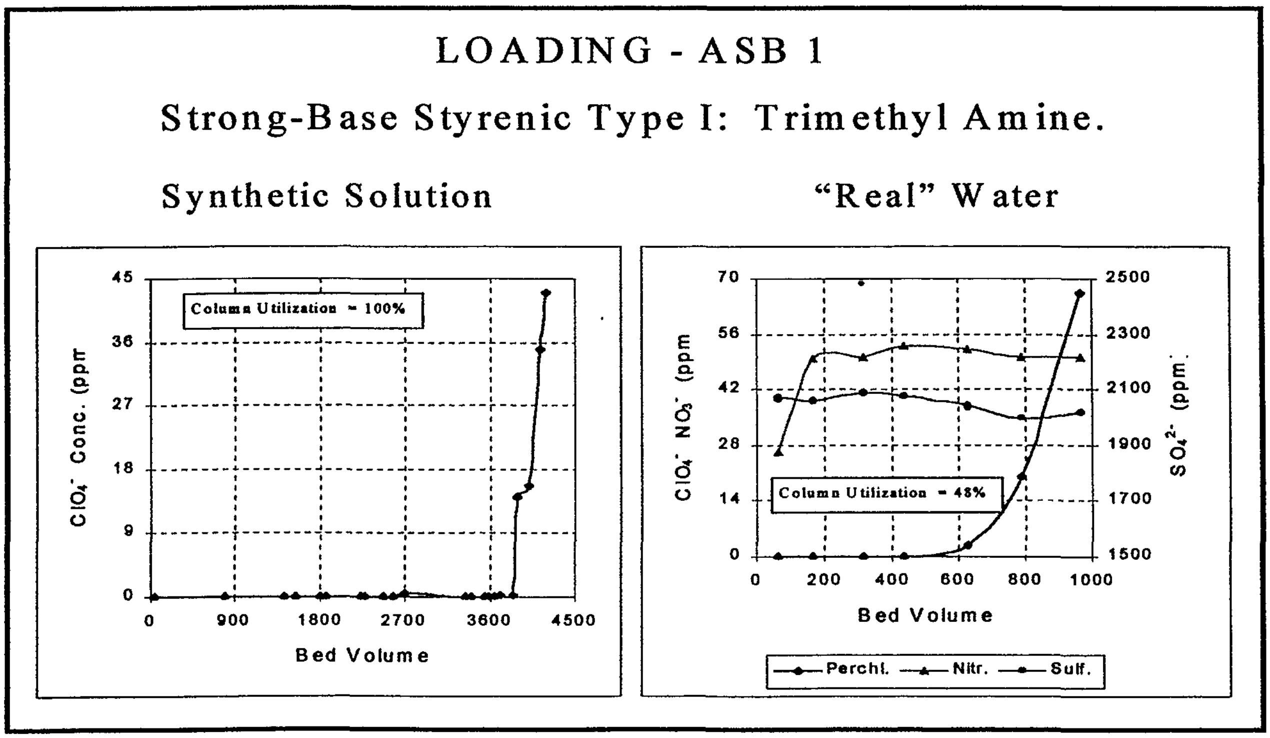

Figure 2: Breakthrough curves for ASB 1 resin loaded with synthetic perchlorate solution and "real" water.

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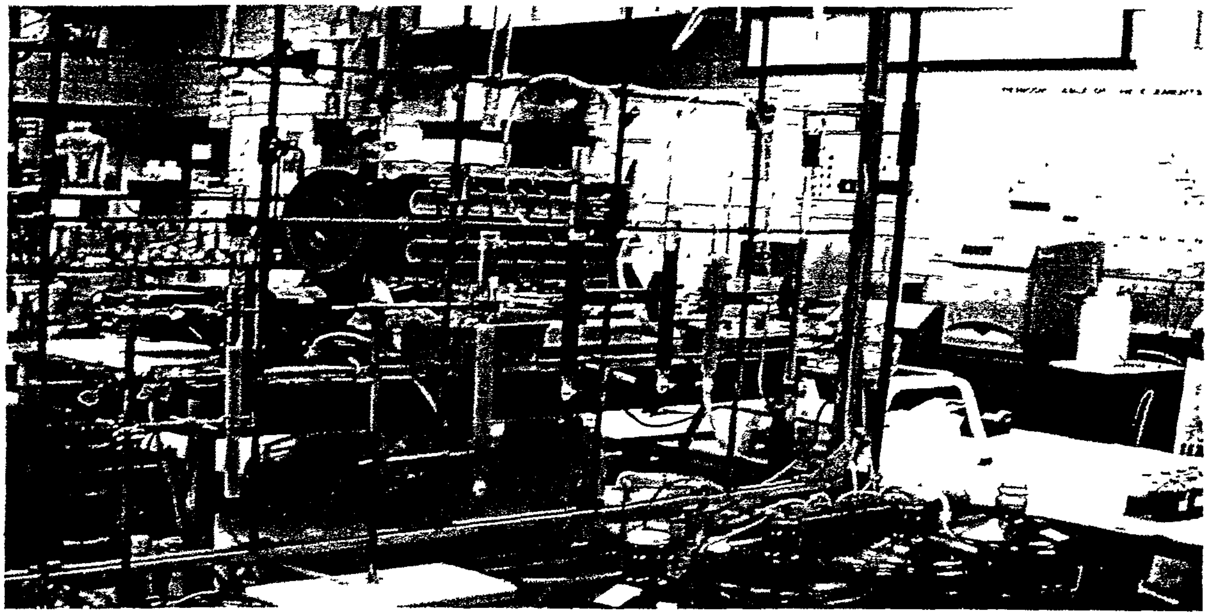

Figure 3

Figure 3: ASB 1 and ASB 2 resins when loaded with synthetic perchlorate solution (yellow resin) and when loaded with the "real" water (dark resin).

The loading of a strong-base styrenic type II resin (Sybron Chemicals – ASB 2) with synthetic perchlorate solution and with the "real" water is shown in Figure 4. Notice that when synthetic perchlorate solution is used 100% of the column capacity is utilized. However, when the "real" water is used the column utilization decreases to 36%. Again, sulfate and nitrate do not exchange at great extent and the resins became dark (Figure 3), indicating the possible presence of humic substances.

Figure 5 shows the results of column testing using styrenic weak base anion exchange resin (Sybron Chemicals AFP 329). Notice that column utilization for this resin using synthetic perchlorate solution and "real" water is very poor (17.8% for the synthetic solution and 16% for the real water). Sulfate and nitrate also did not exchange at all and the resin became a little darker indicating the presumed influence of humic substances.

The loading data for an acrylic strong base resin with a quaternary amine group (Sybron Chemicals - Macro T) is shown in Figure 6. About 56%, which represents more than 1800 bed volumes, of the resin bed was utilized when the synthetic solution was fed to the column. On the other hand, when the "real" water was utilized, no perchlorate could exchange with the resin bed. In addition, sulfate and nitrate did not exchange. These observations suggest that the efficiency of acrylic quaternary amine type resins is significantly affected by the presence of humic substances contained in the "real" water.

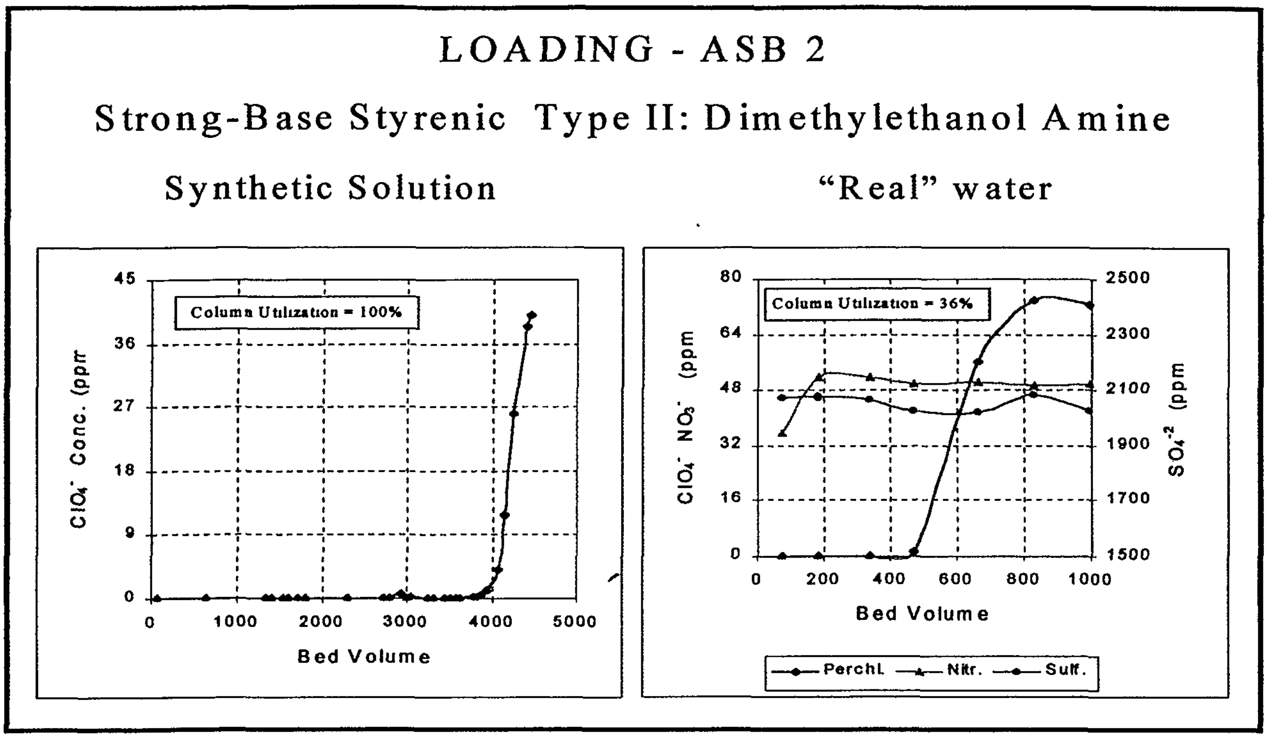

Figure 4: Breakthrough curves for ASB 2 resin loaded with synthetic perchlorate solution and "real" water.

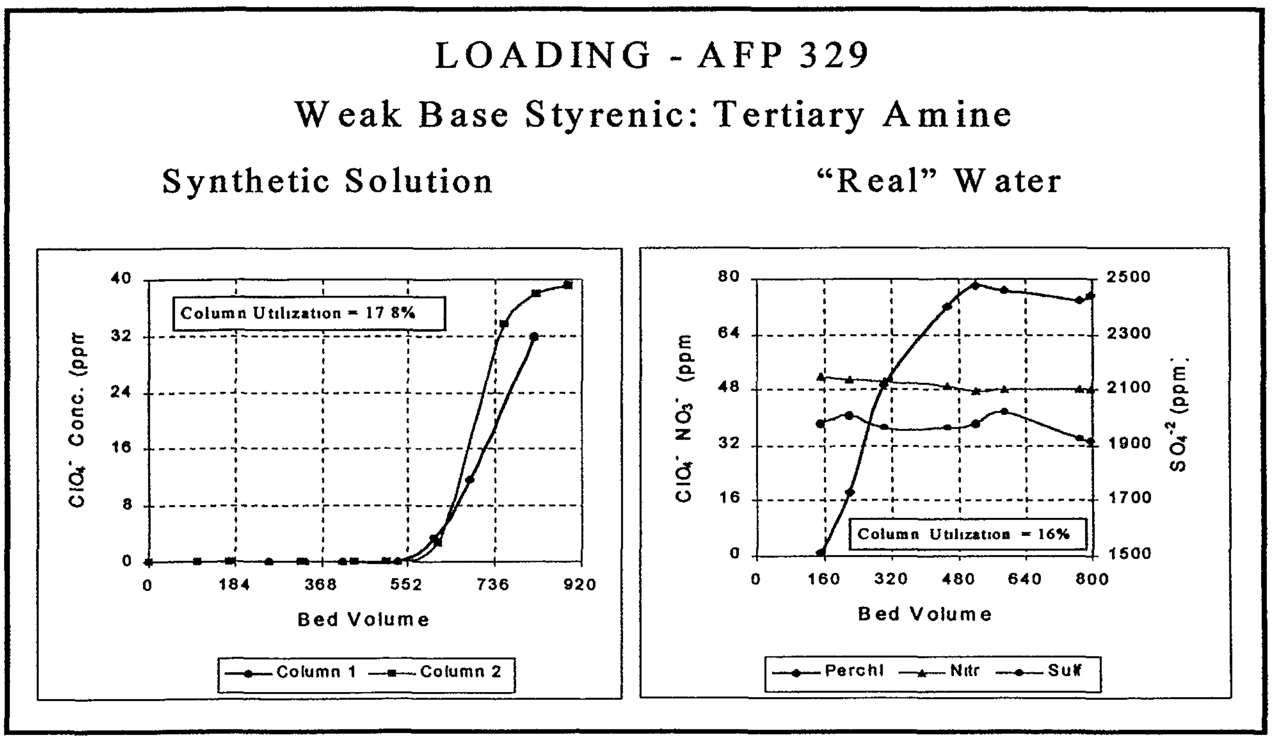

Figure 5: Breakthrough curves for AFP329 resin loaded with synthetic perchlorate solution and "real" water.

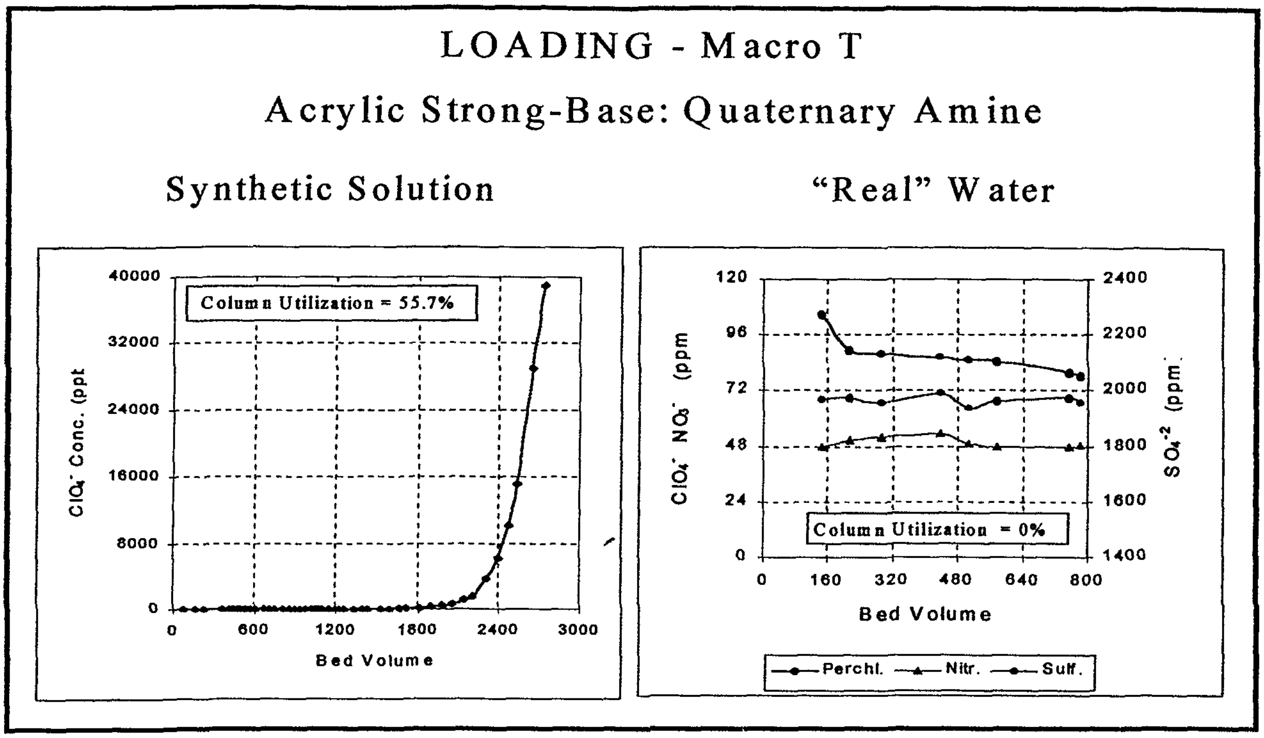

Figure 6: Breakthrough curves for Macro T resin loaded with synthetic perchlorate solution and "real" water.

Figure 7 shows the loading and regeneration for a styrenic strong base anion resin (Sybron Chemicals ASB1 PC) with a quaternary amine functional group. The testing of this resin with synthetic perchlorate solution was not completed on time to report on this paper. Notice that about 21% of the column capacity were utilized by perchlorate and regeneration with 12% NaCl was able to remove 55% of the loaded perchlorate. Again, sulfate and nitrate did not exchange indicating the potential influence of humic substances in the exchange process.

Figure 8 and 9 show the column regeneration for ASB1 and AFP329 using 12% sodium chloride solution. Notice that the regeneration efficiency for the "real" water is lower than that for synthetic perchlorate solution. In addition, the regeneration curves generated from the columns loaded with the "real" water were not very sharp. This indicates that the release of perchlorate and other anions from the resin is hindered. These observations indicate that humic substances also interfere with regeneration efficiency. All columns loaded with the "real" water were regenerated using NaCl 12% and for all resins regeneration was not very effective. The amount of perchlorate recovered varied from 18% (ASB1) up to 55% (ASB1 PC).

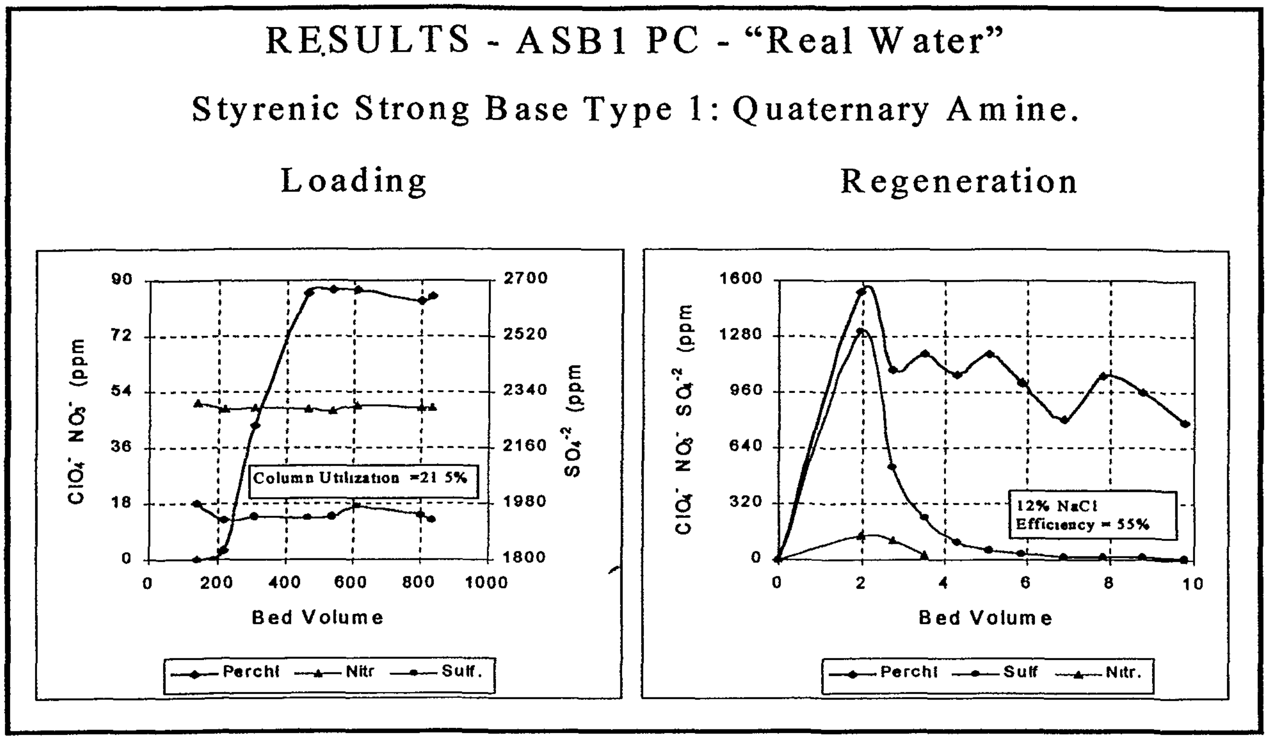

Figure 7: Loading and regeneration of ASB1 PC resin column for perchlorate removal.

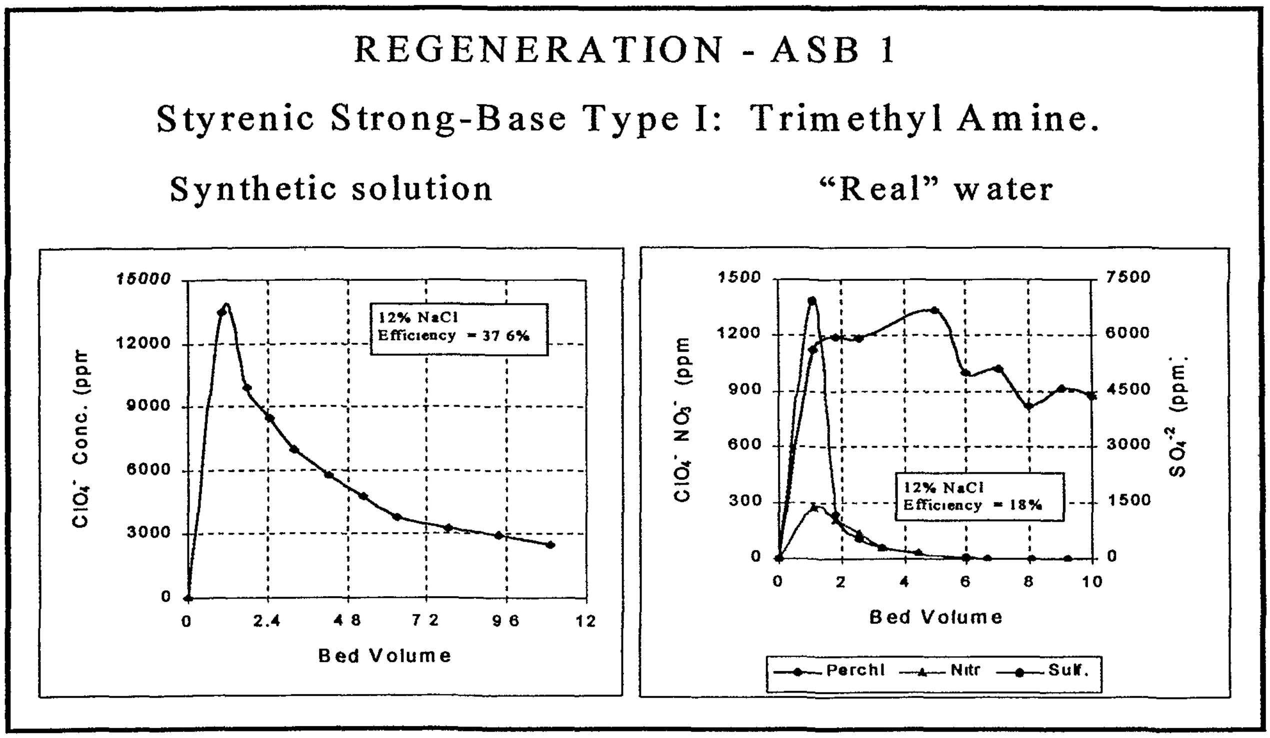

Figure 8: Regeneration curves for ASB 1 resin loaded with synthetic perchlorate solution and "real" water.

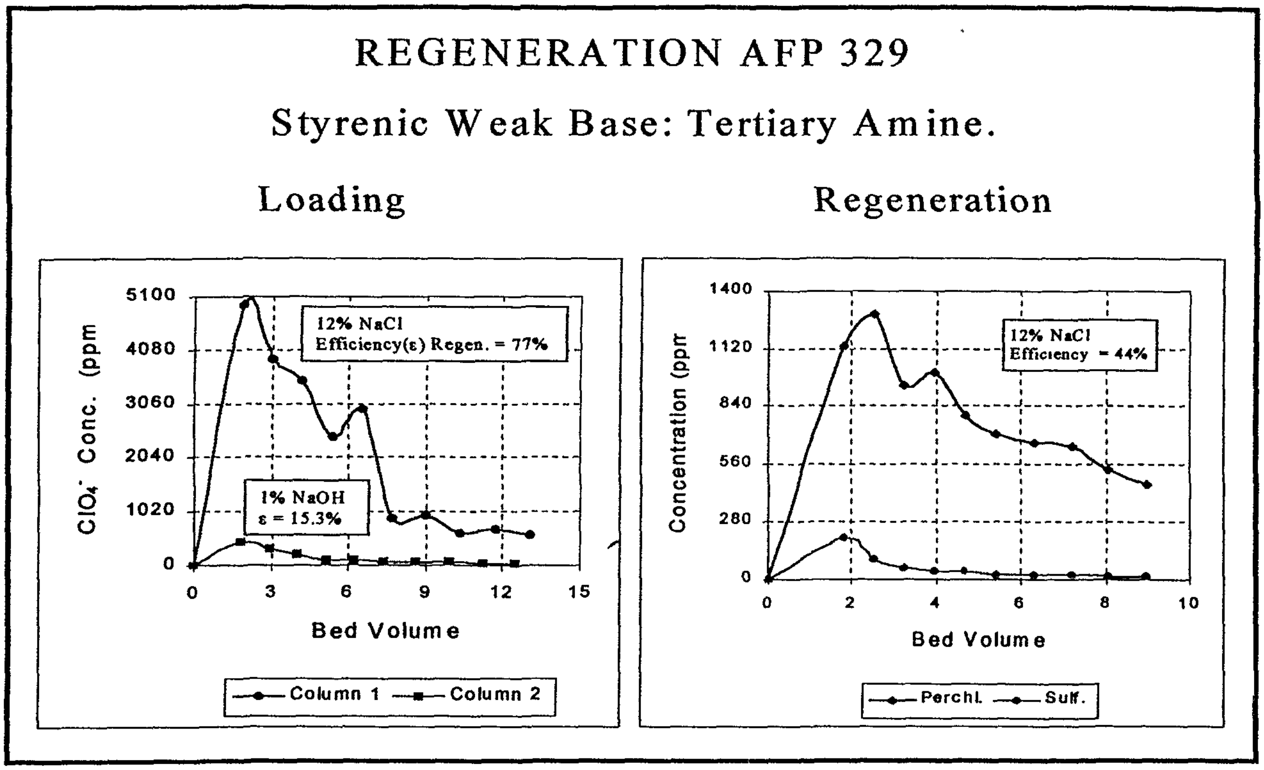

Figure 9: Regeneration curves for AFP 329 resin loaded with synthetic perchlorate solution and "real" water.

CONCLUSIONS

➧ Styrenic strong base resins (ASB1 and ASB2) show very high column utilization for synthetic perchlorate solution. However, for the "real" water only about 40% of the column were utilized. Contrary to expectations, sulfate and nitrate from the "real" water were not exchanged at great extent. It is suspected that most of the resin capacity was taken-up by humic substances.

➧ Acrylic strong base resin with a quaternary amine as functional group (Macro T) has high column utilization for synthetic perchlorate solution and it regenerates very well with NaCl 12%. However, when this resin was loaded with "real" water, perchlorate was not exchanged at all. Neither sulfate nor nitrate could be exchanged with the resins. These observations show that the effects of humic substances seem to be stronger in acrylic than in styrenic resins.

➧ The column utilization for a styrenic strong base macroporous resin (ASB1 PC) was lower than that for a "non"-porous styrenic strong base resin (ASB1). This was unexpected, since ASB1 PC is a macroporous resin and it is supposed to be resistant to organic fouling.

➧ Styrenic weak base resin (AFP 329) has shown low, but approximately the same column utilization for the "real" water and for the synthetic perchlorate solution. Sulfate and nitrate were not exchanged at all.

➧ Humic substances may greatly interfere with the removal of perchlorate from waters. Investigation is needed to determine the influence of different levels of humic substances on the removal of perchlorate from waters.